



**Experiment title:** Characterization, by means of  $\mu$ -XRF and  $\mu$ -XANES, of Fe-oxides and -oxyhydroxides formed by polymetallic sulphides alteration during AMD processes

**Experiment number:**  
EC-156

**Beamline:**  
ID21

**Date of experiment:**  
from: 19-APR-2007 to: 24-APR-2007

**Date of report:**  
29 february 2008

**Shifts: 15**

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*Received at ESRF:*

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## Report:

We report preliminary results obtained using  $\mu$ -XRF and  $\mu$ -XANES analyses, performed at the ID21 beamline, on Fe-oxides and -oxyhydroxides bearing samples formed by polymetallic sulphides alteration during AMD (Acid Mine Drainage) processes at the Libiola Mine (Sestri Levante, Genova, Italy).

The samples were the same used for a previous experiment (CH-2095, ID18F) that allowed to determine the mineralogy (by  $\mu$ -XRD) and the elemental concentration (by  $\mu$ -XRF; for elements with  $Z > 26$ ) along several transects containing the transition from unaltered sulphides to completely altered Fe-oxides and -oxyhydroxides layers

During the experiment EC-156 we focused the attention on three different samples: a) the first sample is characterized by a well defined transition from an unaltered massive mineralization (pyrite  $\pm$  chalcopyrite  $\pm$  sphalerite) to the surrounding oxidation products (Fig. 1a); b) the second sample is a weakly altered stockwork mineralization (pyrite  $\pm$  chalcopyrite) consisting of a complex network of sulphide veins surrounded by a silicate matrix (dark green) and crosscutted by Fe-oxyhydroxides veins (ochreous veins). c) the third sample is a stratified hardpan consisting of rhythmic alternation of submillimetric hematite-rich (red) and goethite-rich (ochreous) layers (Fig. 1c).

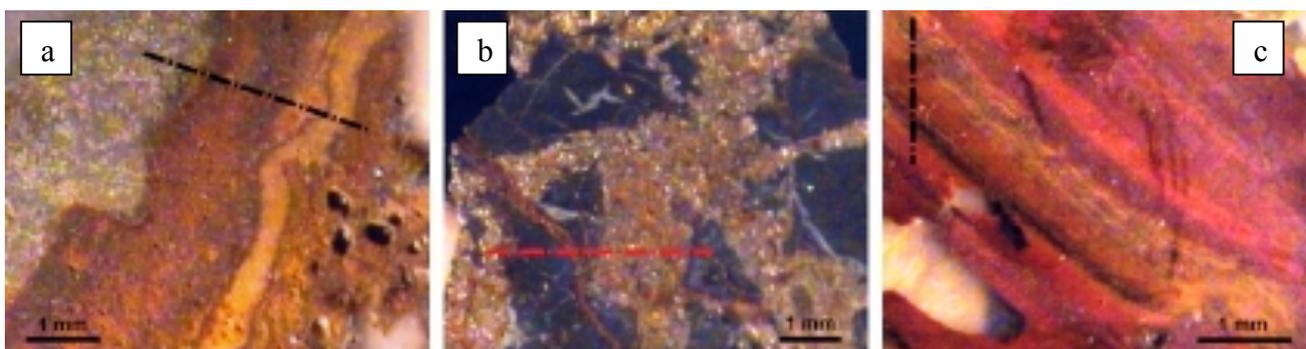


Fig. 1: Optical microscopy images of the investigated samples: a) analysed transect (dashed line) along the transition from unaltered sulphide mineralizations (grey part on the left) to Fe-oxide and -oxyhydroxides bearing layer (ochreous-reddish part on the right). b) analysed transect (dashed line) along a stockwork sulphide mineralization (grey veins) surrounded by silicate matrix (dark green) and crosscutted by Fe-oxyhydroxides veins (ochreous veins). c) stratified hardpan consisting of rhythmic alternation of submillimetric hematite-rich (red) and goethite-rich (ochreous) layers.

On the three samples we performed micro-XANES and micro-XRF maps along selected transects (Fig. 1a-c); the maps were carried out in areas of  $100 \times 100 \mu\text{m}$  with a resolution of  $1 \times 1 \mu\text{m}$ . The sulphur oxidation state were determined by scanning the energy of the exciting beam across the sulphur absorption K-edge (Total S = 2.55 KeV; sulphide = 2.472 KeV; sulphate = 2.482 KeV). The exciting energy for micro-XRF maps and profiles was set to maximise the fluorescence yield of the elements with  $13 \leq Z < 26$ .

XANES maps have been performed to follow the steps of pyrite alteration (Fig. 2-3) Preliminary results evidenced that the first step is marked by sulphur oxidation to sulphate. This oxidation process starts from the crystals rims or from intragrain microfractures (Fig.2c) Sulphate is then rapidly leak out from the system and few  $\mu\text{m}$  within the outer altered layers is almost completely absent.

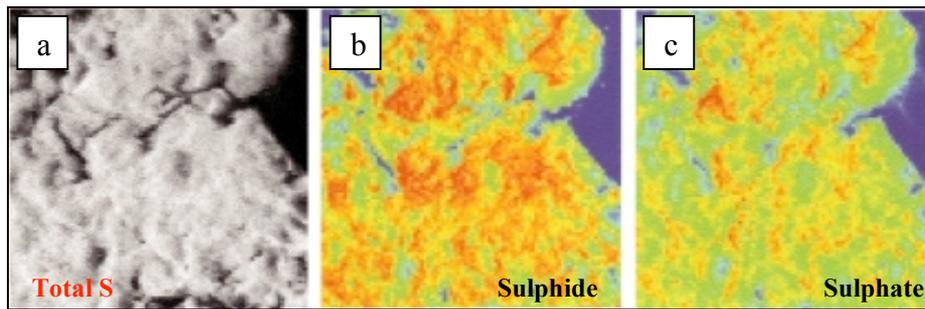


Fig. 2: XANES maps (temperature scale: red = highest concentration, blue = lowest concentration) of a) total S, b) sulphide, and c) sulphate distribution in idiomorphic pyrite crystals (stockwork mineralizations). Map area = 100 x 100  $\mu\text{m}$ .

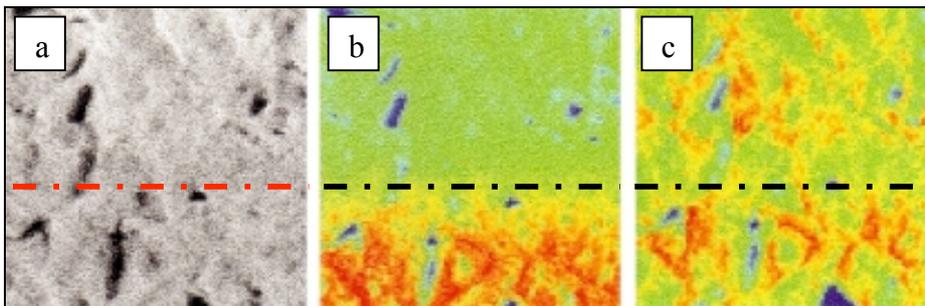


Fig. 3: XANES maps (temperature scale: red = highest concentration, blue = lowest concentration) of a) total S, b) sulphide, and c) sulphate distribution along the transition area from massive mineralization (below dashed line) to Fe-oxide and -oxyhydroxides layer (above dashed line). Map area = 100 x 100  $\mu\text{m}$ .

The altered layers, composed almost exclusively by Fe-oxides (hematite) and -oxyhydroxides (goethite, ferrihydrite, lepidocrocite), concentrically rim crystals, and fill intra- and inter-grain interstices. Elemental maps and  $\mu\text{-XRF}$  transects confirmed the high affinity of the secondary minerals to adsorb or incorporate many of the elements leached from sulphides or from gangue minerals, and thus their very important role on the control of the mobility of trace contaminants. In particular, we constantly observed significant enrichment in Cr in the hematite and goethite rich layers (Fig. 4-5) as well as good positive correlations between Fe and Al, Mn, Ti, and V. Moreover,  $\mu\text{-XRF}$  maps confirm the strong depletion of sulphur in the Fe-oxides and -oxyhydroxides. Further studies are in progress to complete the data set interpretation and to combine the present results with those of experiment CH-2095. Moreover, S and Fe K-edge XANES data, collected on selected regions, will be analyzed to get more accurate information on the S and Fe oxidation states and local structure in these regions.

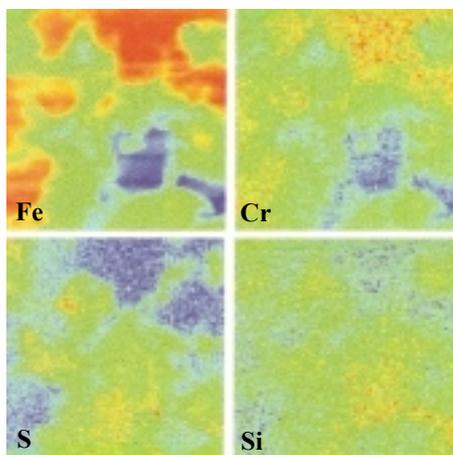


Fig.4: elemental concentration maps (temperature scale: red= highest concentration, blue = lowest concentration) for Fe, Cr, S, and Si on a 100x100  $\mu\text{m}$  window across the transition zone of sample 1 (Fig1a)

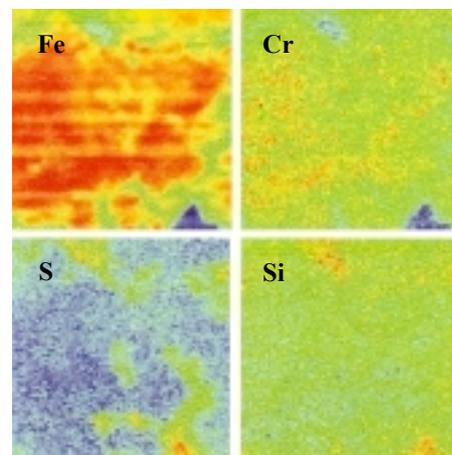


Fig.5: elemental concentration maps (temperature scale: red = highest cocentration, blue = lowest concentration) for Fe, Cr, S, and Si on a 100x100  $\mu\text{m}$  window across a completely altered pyrite crystal (sample 2; Fig1b)